P154755.PDF [Page: 3 of 66]

UNCLASSIFIED

DEFENCE RESEARCH ESTABLISHMENT
CENTRE DE RECHERCHES POUR LA DÉFENSE
VALCARTIER, QUÉBEC

DREV - R - 9512

LIMITED DISTRIBUTION/DISTRIBUTION LIMITÉE

CHARACTERISTICS OF SECOND GENERATION BRANCHED GAP

by

E. Ahad

December/décembre 1995

Approved by/approuvé par

Director/Directeur

17/11/95
Date

SANS CLASSIFICATION

ABSTRACT

This report describes the solution properties and thermal characteristics of second generation branched glycidyl azide polymer (GAP). The GAP products obtained in different solvents have the same viscosity-molecular weight and functionality-molecular weight relationships. The properties of branched GAP synthesized without using any polyol in the reaction and the characteristics of the polymers prepared without cleaving agent are also reported. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) thermograms, the glass transition temperature (Tg) as well as the heats of combustion (ΔH_c), formation (ΔH_f) and decomposition (ΔH_d) of branched GAP are also presented. The correlation between the vacuum thermal stability (VST) of the GAP product and the synthesis parameters is also discussed. The effects of stabilizers, additives and the purification procedure (extraction or water precipitation) on the properties of the GAP product are also investigated.

RÉSUMÉ

Ce rapport décrit les propriétés en solution et les caractéristiques thermiques du polyazoture de glycidyle (PAG) ramifié de seconde génération. Les produits PAG obtenus dans différents solvants ont des relations similaires entre la viscosité et la masse moléculaire et entre la fonctionnalité et la masse moléculaire. On rapporte également les propriétés du PAG ramifié synthétisé sans utiliser de polyol dans la réaction et les caractéristiques des polymères préparés sans agent de clivage. On présente aussi les thermogrammes d'analyse thermique différentielle (DTA) et d'analyse thermogravimétrique (TGA), la température de transition vitreuse (Tg) ainsi que les chaleurs de combustion (ΔH_c), de formation (ΔH_f) et de décomposition (ΔH_d) du PAG ramifié. On discute également de la corrélation entre la stabilité thermique sous vide (VST) du PAG et des paramètres de synthèse. On examine aussi les effets de stabilisateurs, d'additifs et de la méthode de purification (extraction ou précipitation dans l'eau) sur les propriétés du produit PAG.

P154755.PDF [Page: 7 of 66]

PRECEDING PAGE BLANK

TABLE OF CONTENTS

ABSTRACT/RÉSUMÉ i

EXECUTIVE SUMMARY v

NOMENCLATURE vii

1.0 INTRODUCTION 1

2.0 EXPERIMENTAL 1

2.1 Branched GAP Samples 1
2.2 Solution Properties 2
2.3 Thermal Properties 2

3.0 RESULTS AND DISCUSSION 3

3.1 Solution Properties of Second Generation Branched GAP 3
3.2 Properties of Branched GAP Synthesized without Polyol 4
3.3 Properties of Branched GAP Synthesized without Cleaving Agent .. 5
3.4 Thermal Properties of Second Generation Branched GAP 6
3.5 Effect of Purification Procedure 10
3.6 Effect of Stabilizers and Additives 12

4.0 CONCLUSIONS 15

5.0 ACKNOWLEDGEMENTS 16

6.0 REFERENCES 17

TABLES I to XVII

FIGURES 1 to 9

P154755.PDF [Page: 9 of 66]

PRECEDING PAGE BLANK

EXECUTIVE SUMMARY

Glycidyl Azide Polymer (GAP) is a potential energetic binder for rocket propellants with reduced smoke and low vulnerability as well as for insensitive composite explosives and gun propellants. For these reasons, GAP is considered as an attractive substitute for the inert hydroxy-terminated polybutadiene conventional binder currently used in many energetic formulations such as the CRV-7 Rocket and plastic-bonded explosives.

GAP currently produced in the USA is relatively expensive and is prepared according to a two-step process involving two distinct chemical reactions. In 1987, a process was discovered at DREV for the preparation in a single step of first generation Canadian branched GAP by reacting a polyepichlorohydrin (PECH) rubber with epichlorohydrin (ECH) monomer and sodium azide.

Recently, an improved process has been developed and patented by DREV for the preparation of second generation branched GAP in one step but without the addition of an epoxide monomer such as ECH. The chemical reaction has been simplified in this novel process which involves both the degradation and azidation of an inexpensive commercial rubbery PECH with sodium azide in the presence of a base (optional) and a polyol (optional) for a few hours at elevated temperature. Besides, this process is versatile since the molecular weight, viscosity and hydroxyl content of the product may be controlled by varying the relative proportions of the reactants.

The purpose of this study is to describe the solution properties and thermal characteristics of second generation branched GAP as well as the effects of stabilizers, additives and the purification procedure on the properties of the product.

The technology of this process has been transferred to ICI Explosives Canada under the Defence Industrial Research (DIR) Program to design and build a pilot-plant to produce development quantities of branched GAP for testing, to select suitable industrial equipment and to obtain a reliable estimate about the cost of GAP manufacturing. A pilot plant was built at McMasterville with a capacity of 25 kg per week and has been producing since 1993 batches of second generation branched GAP with good properties.

P154755.PDF [Page: 11 of 66]

PRECEDING PAGE BLANK

NOMENCLATURE

CH_3OLi	lithium methoxide
CH_3ONa	sodium methoxide
DBHQ	di-ter-butyl hydroquinone (stabilizer)
DMA	dimethyl acetamide
DMF	dimethyl formamide
DMSO	dimethyl sulfoxide
DSC	differential scanning calorimetry
DTA	differential thermal analysis
EG	ethylene glycol
f	hydroxyl functionality (average number of OH groups per molecule)
GAP	glycidyl azide polymer
ΔH_c, ΔH_d, ΔH_f	heat of combustion, decomposition and formation, respectively
HT	hexanetriol
LiCℓ	lithium chloride
Li_2S	lithium sulfide
Me	hydroxyl equivalent weight
MW	molecular weight
M_N, M_W	number and weight average molecular weight, respectively
NaN_3	sodium azide
NaOH	sodium hydroxide
PE	pentaerythritol
PECH	polyepichlorohydrin
PEG	polyethylene glycol
Quinol	hydroquinone (stabiliser)
Santonox	commercial stabilizer [4,4'-thio-bis(6 ter-butyl-m-cresol)]
Tg	glass transition temperature
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMP	trimethylol propane
TP	triphenyl phosphine (stabilizer)
VST	vacuum thermal stability
η, $[\eta]$	absolute and intrinsic viscosity, respectively

1.0 INTRODUCTION

An improved and versatile process was developed and patented recently by DREV (Refs. 1-3) for the synthesis in a single step of second generation branched GAP with controlled and variable molecular weight (MW 1000-200,000). This process involves the simultaneous azidation and degradation of a cheap commercial rubbery polyepichlorohydrin (PECH) with sodium azide in the presence of a basic cleaving agent and a polyol in a polar organic solvent for a few hours at elevated temperature; the cleaving agent and/or the polyol are optional. The MW, viscosity, equivalent weight and hydroxyl functionality of the GAP product can be controlled and predetermined by varying the relative proportions of the ingredients in the reaction mixture.

The technology of this process has been transfered to ICI Explosives Canada under the Defence Industrial Research (DIR) program (Refs. 4-7). The process scale-up has been achieved at the DREV Experimental Complex (Ref. 8) and the pilot plant of ICI at McMasterville leading to the production of development quantities of second generation branched GAP for evaluation and testing.

The method of synthesis of second generation branched GAP as well as the effect of reaction parameters on the properties of the product were described in a previous report (Ref. 9). The object of this report is to present the solution and thermal properties of second generation branched GAP as well as the effects of stabilizers, additives and the purification procedure on the properties of the product.

This work was performed at DREV between September 1989 and June 1994 under PSC 32C, Rockets and Missiles.

2.0 EXPERIMENTAL

2.1 Branched GAP Samples

The branched GAP samples used in this study were obtained by the degradation process described in Ref. 9. The polymers were prepared at elevated temperature (90-120°C) in different solvents and using various polyols and cleaving agents. Some syntheses were also carried out without polyol and/or cleaving agent and, in some cases, stabilizers and additives were included in the reaction in order to study and assess the effects of these reactants and ingredients on the properties of the branched GAP product.

P154755.PDF [Page: 14 of 66]

2.2 Solution Properties

The weight average molecular weight (M_W), number average molecular weight (M_N), hydroxyl equivalent weight (Me), hydroxyl functionality (f) and absolute viscosity (η) of second generation branched GAP were determined according to the techniques reported in Ref. 9. The intrinsic viscosity [η] values were measured at 25°C in tetrahydrofuran (THF) using an Ubbelohde capillary viscometer.

2.3 Thermal Properties

2.3.1 Calorimetry

The heat of combustion (ΔH_c) of branched GAP was determined with a Parr adiabatic oxygen bomb calorimeter (model 1241); the calculations were carried out according to the procedure described in Ref. 10. The heat of formation (ΔH_f) was calculated from the value found for ΔH_c and according to the following thermochemical equation:

$$C_3H_5ON_3 + \frac{15}{4}\,O_2 \rightarrow 3CO_2 + \frac{5}{2}\,H_2O + \frac{3}{2}\,N_2$$

The differential thermal analysis (DTA), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of branched GAP were carried out with a Dupont (2100 TA) instrument at a heating rate of 10°C/min. The glass transition temperature (Tg) and the heat of decomposition (ΔH_d) were determined by DSC.

2.3.2 Thermal Stability

The vacum thermal stability (VST) of branched GAP was determined according to the standardization agreement STANAG 4147 of NATO (Ref. 11) using Method 503.1 of MIL-STD 650 (Ref. 12). The test was carried out at a temperature of 100°C over a period of 48 h, as recommended by the US Navy (Refs. 13-14). For such a test, a compound is considered stable if the amount of gas evolved does not exceed 2 mL/g.

3.0 RESULTS AND DISCUSSION

3.1 Solution Properties of Second Generation Branched GAP

The solution properties of second generation branched GAP are presented in Tables I, II and III for the samples prepared respectively in Dimethyl Sulfoxide (DMSO), Dimethyl Acetamide (DMA) and Dimethyl Formamide (DMF). The variation of log [η] versus log M_W was plotted in Fig. 1 for all these samples. The following Mark-Houwink relation was calculated from the curve drawn in Fig. 1 for second generation branched GAP in tetrahydrofuran (THF):

$$[\eta] = 2.80 \text{ X } 10^{-4} M_W^{0.62}$$

This relationship holds for the samples prepared in DMSO as well as for those synthesized in DMA and DMF; this is an indication that the branched GAP samples obtained in different reaction solvents have similar hydrodynamic volumes.

As shown in Tables I, II and III, the molecular weight (MW) distribution increases with the MW of the GAP product. The polydispersity index (M_W/M_N) is approximately 1.8 for low MW samples (M_W = 2000-8000) and increases to about 3.5 for high MW samples (M_W ~ 168,000). The hydroxyl equivalent weight (Me) and hydroxyl functionality (f) increase also with the MW of the GAP product; samples with low M_N (1400-2200) have low values for Me (600-960) and functionality (f = 2.3), whereas samples with high M_N (48,000) have relatively higher values for Me (3800) and functionality (f = 12.6).

The fact that the hydroxyl functionality increases with the MW of the GAP product is an indication that the degree of branching and the average number of OH groups per molecule increase with the polymer chain length. The variation of f versus M_N was plotted in Fig. 2 for all the branched GAP samples synthesized in DMSO, DMA and DMF. The following MW-functionality relationship was calculated from the curve drawn in Fig. 2:

$$f = 1.75 + 2.33 \text{ X } 10^{-4} M_N$$

The results presented in Tables I, II and III also indicate that the absolute viscosity increases with the MW of the GAP product. A graph of log $\eta_{25°C}$ versus log M_W was plotted in Fig. 3 for all the GAP samples prepared in DMSO, DMA and DMF. The following empirical relations were calculated from the curve drawn in Fig. 3 for different MW ranges:

P154755.PDF [Page: 16 of 66]

for Mw < 30,000 :

$$\log \eta_{25°C} = 0.76 \log M_W + 1.59$$

for Mw > 30,000 :

$$\log \eta_{25°C} = 2.05 \log M_W - 4.18$$

These relations hold for all the branched GAP samples prepared in different reaction solvents.

3.2 Properties of Branched GAP Synthesized without Polyol

The properties of some second generation branched GAP samples prepared without using polyols in the reaction are listed in Table IV. All the samples were obtained in DMSO after 16 h at 120°C using CH_3OLi as the basic cleaving agent. The method of synthesis is similar to the one reported in Ref. 9, except that the polyol is omitted. As shown in Table IV, the values of η, M_W and Me are reduced when the CH_3OLi concentration is increased in the reaction mixture as observed in the case of reactions involving polyols reported in Ref. 9. The functionality values are below 10 and vary with the MW as was the case for the branched GAP products obtained by using polyols in the synthesis reactions.

A comparison of the properties of two branched GAP samples, N75 and N95, prepared respectively with and without polyol are presented in Table V. The two samples were obtained in the same experimental conditions except for the polyol. Both samples were synthesized in DMSO for 16 h at 120°C with a similar cleaving agent concentration (CH_3OLi/PECH = 0.03). However, Sample N75 was prepared by including in the reaction trimethylol propane (TMP) as polyol with a concentration TMP/PECH = 0.25, whereas Sample N95 was obtained without using any polyol in the synthesis reaction.

As shown in Table V, Sample N95 (synthesized without polyol) has higher values for M_W, M_N, (M_W/M_N) and η compared with Sample N75 (prepared with TMP). This is an indication that the addition of a polyol into the reaction mixture enhances the reactivity of the cleaving agent and causes a further reduction in the MW and viscosity of the GAP product. Sample N95 has also a higher value for Me and a lower functionality compared to Sample N75 indicating that additional OH groups (originating from the polyol) are incorporated into the GAP molecular structure when a polyol is used in the reaction. These findings corroborate those reported in Ref. 9 regarding the polyol effects on the MW and hydroxyl content of the GAP product.

A comparison of the functionality distribution of Samples N75 and N95 is also presented in Table V. The functionality distribution was determined from the MW-functionality relationship established in Section 3.1 and the MW distribution obtained from the GPC chromatograms of these two samples shown in Fig. 4. Sample N75 (prepared with TMP) has a lower proportion (38.4 wt %) of hydroxyl functionalities above 3.5 compared with Sample N95 (51.5 wt %) obtained without polyol. On the other hand, 59.3 wt % of Sample N75 have a functionality between 2 and 3.5 in comparison with 46.3 wt % in the case of Sample N95. Both samples contain however the same proportion (approx. 2.3 wt %) of functionalities below 2. Therefore, branched GAP samples synthesized without using any polyol in the reaction will have a different distribution of hydroxyl functionality than those obtained from reactions involving polyols. This will have a noticeable effect on the mechanical properties of the energetic binders formulations as reported in Refs. 15, 16 and 17.

3.3 Properties of Branched GAP Synthesized without Cleaving Agent

The properties of some second generation branched GAP samples prepared without using a basic cleaving agent in the reaction are listed in Table VI. All the samples were obtained in DMSO after 16 and 32 h at reaction temperatures of 100 and 120°C. Samples N94, N96 and N103 were prepared by including in the reaction TMP and pentaerythritol (PE) as polyols with a weight ratio (Polyol/PECH) = 0.25. The method of synthesis of these samples is similar to the one reported in Ref. 9, except that the cleaving agent is omitted. Sample N113 was prepared without using any polyol in the reaction according to the synthesis method described in Ref. 9, except that the cleaving agent and the polyol were omitted.

As shown in Table VI, the branched GAP samples have a relatively higher MW (M_w = 85,000-174,000), viscosity (η = 690,000-2.6 X 10^6 cP) and hydroxyl functionality (f above 10) in comparison with the products (MW < 40,000 and f < 10) of reactions involving basic cleaving agents reported in Ref. 9. The use of a polyol in the reaction caused a reduction in the viscosity of the product: Sample N94 (η = 96,200 cP) prepared with TMP had a lower viscosity than Sample N113 (η = 1.48 X 10^6 cP) synthesized without polyol. These viscous branched GAP samples with high MW obtained without cleaving agents can be used in the preparation of energetic thermoplastic elastomers, as reported in Ref. 18.

P154755.PDF [Page: 18 of 66]

3.4 Thermal Properties of Second Generation Branched GAP

3.4.1 Glass Transition Temperature

The glass transition temperature (Tg) of various second generation branched GAP samples are listed in Table VII along with their corresponding values of M_w and f. The branched GAP samples were synthesized in DMA and DMSO with different polyols using CH_3OLi as cleaving agent; a couple of branched GAP samples (N95 and E261) were also prepared without polyol. The results of a commercial linear GAP diol supplied by 3M Comp. are also presented in Table VII for comparison purposes.

The results of Table VII indicate that the second generation branched GAP samples have Tg values of -46 ± 5°C, comparable with the Tg (-45 °C) value found for the linear GAP diol. However, the branched GAP samples have a relatively higher M_w (above 10,000) and hydroxyl functionality (above 3) compared with the linear GAP sample (M_w = 2250, f = 1.5).

As shown in Table VII, the reaction solvent and the polyol co-reagent had no significant effect on the Tg of second generation branched GAP. However, the Tg value seems to vary slightly with the MW and hydroxyl functionality of the product. The branched GAP with relatively low M_w (9000-13,000) and functionality (3.0 - 3.7) have a Tg of -44 ± 2°C, whereas the samples with higher M_w (17,000-81,000) and functionality (3.8-11.2) have a Tg of -49 ± 2°C. As the functionality generally increases with the MW, consequently a GAP sample with a higher degree of branching will have a slightly lower Tg than the sample with lower functionality and MW.

3.4.2 Heats of Combustion, Formation and Decomposition

The heats of combustion (ΔH_c) and formation (ΔH_f) of some second generation branched GAP samples synthesized in DMA and DMSO are listed in Table VIII. The GAP samples obtained in DMA were prepared by using glycerol and ethylene glycol (EG) as polyols and NaOH and CH_3OLi as cleaving agents, whereas the samples obtained in DMSO were synthesized with glycerol and CH_3OLi.

The results of Table VIII indicate that the synthesis solvent and the polyol co-reagent had no significant effect on the heat of combustion of branched GAP, whereas the cleaving agent used in the reaction had a slight effect on ΔHc. The GAP samples synthesized with CH_3OLi (ΔH_c = -4952 ± 1.3 % cal/g) had slightly higher heat of combustion values than those prepared with NaOH (ΔH_c = -4875 ± 0.8 % cal/g). Although this difference observed for the heat of combustion is minor and within experi. ental error, it becomes more noticeable for the heat of formation. As shown in Table VIII, a variation as small as ± 15 cal/g (about ± 0.3 %) in the heat of

P154755.PDF [Page: 19 of 66]

combustion value for a given sample will cause a variation in the corresponding heat of formation of that same sample of ± 1.5 kcal/mole which represents approximately 4-5 %. Nevertheless, the branched GAP samples prepared with NaOH (ΔH_f = +29.9 ± 13 % kcal/mole) had generally lower heat of formation values compared with the samples synthesized with CH_3OLi (ΔH_f = + 37.5 ± 17 % kcal/mole).

The heat of decomposition (ΔH_d) and the peak temperature (T_p) of some second generation branched GAP samples are listed in Table IX. The results obtained for a commercial linear GAP diol are also presented in this table for comparison purposes. The branched GAP samples were synthesized in DMA and DMSO using CH_3OLi as cleaving agent; the samples prepared in DMA were obtained after 32 h at 100°C using EG as polyol, whereas the samples prepared in DMSO were obtained after 16 h at 120°C with hexanetriol (HT), pentaerythritol (PE) and without polyol.

The results of Table IX show that the second generation branched GAP samples have values of ΔH_d = 490 ± 15 % cal/g and T_p = 253 ± 2°C. The heat of decomposition and peak temperature of branched GAP are thus comparable with the results determined for the linear GAP diol (ΔH_d = 523 cal/g, T_p = 254°C). A typical decomposition thermogram for Sample E38 is shown in Fig. 5. As shown in Table IX, the synthesis parameters (reaction solvent, time, temperature, polyol etc.) had no significant effect on the values of ΔH_d and T_p of the branched GAP product.

3.4.3 Thermal Analysis

Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) of second generation branched GAP were carried out over a temperature range from 20°C to 550°C. Typical DTA and TGA thermograms of Samples E133 and E147 are shown in Figs. 6-9. Samples E133 and E147 were obtained after 32 h in DMSO at 100°C and 90°C, respectively, using glycerol as polyol and CH_3OLi as cleaving agent.

As shown in the DTA thermogram of Sample E133 in Fig. 6, branched GAP appears to be fairly stable up to 175°C when decomposition begins slightly and then amplifies as the temperature is increased. The exothermic peak observed between 200°C and 270°C is attributed to the decomposition of the azide groups in GAP and the release of gaseous nitrogen. The TGA thermogram of 12 mg of Sample E133 shown in Fig. 7 indicates that nearly 87 % of the weight loss occurs in the temperature range 200-270°C, which corresponds to the exothermic DTA peak observed for that sample in Fig. 6.

However, in some cases and depending on the selected experimental conditions (such as sample weight), the TGA thermogram consisted of a two-stage weight loss process. The TGA thermogram in Fig. 8 obtained with 7 mg of Sample E147 indicates that about 36 % of the weight loss occurred between 200°C and 270°C in a first stage. The weight reduction then proceeded more slowly in a second stage as the temperature increased from 270°C to 550°C. When the TGA experiment of Sample E147 was repeated in Fig. 9 but this time with a higher amount of polymer (11 mg), the thermogram represented 90 % weight loss in a single stage process and was thus similar to the thermogram obtained for 12 mg of Sample E133 in Fig. 7.

Kubota et al (Ref. 19) reported that the TGA thermogram of linear GAP diol consisted of a two-stage decomposition process. However, the amount of sample tested was not disclosed. On the other hand, the TGA thermogram obtained at DREV (Ref. 20) for 10 mg of linear GAP diol (lot 1000-5-2) supplied by Rockwell, indicated a single stage decomposition. Consequently, the shapes of the TGA thermograms of branched and linear GAP seem to depend on the weight of the sample used in the experiment.

3.4.4 Vacuum Thermal Stability

The VST values of several second generation branched GAP samples prepared in DMSO and DMA are listed respectively in Tables X and XI along with the values of M_N, the reaction temperature as well as the concentrations of polyol and cleaving agent used in the synthesis. The purification of all the branched GAP samples was achieved according to the extraction procedure described in Ref. 9. The VST results of some linear GAP samples and first generation branched GAP are also presented in Table XII for comparison purposes.

As shown in Table X, all the second generation branched GAP samples obtained in DMSO have a good thermal stability since their VST values are ≤ 2 ml/g. Nevertheless, there is a correlation between the VST values of the branched GAP samples synthesized in DMSO and the cleaving agent concentration used in the synthesis reaction. The samples prepared with a high ratio (cleaving agent/PECH) = 0.05-0.10 have a VST of 1.8 ± 0.2 ml/g, whereas the samples synthesized with a ratio (cleaving agent/PECH) = 0.032-0.045 have a VST of 1.1 ± 0.3 ml/g. On the other hand, the samples obtained at a low ratio (cleaving agent/PECH) = 0-0.030 have a VST of 0.5 ± 0.2 ml/g. Consequently, the branched GAP samples prepared with lower cleaving agent concentrations have relatively lower VST values than the samples obtained at higher concentrations. Since the degradation rate is generally enhanced when the cleaving agent proportion is increased in the reaction mixture, the samples which undergo lesser degradation are relatively more stable than those produced via extensive chain scission. As reported in Ref. 9, mild degradation occurs ideally when

the reaction is conducted without cleaving agent but the product thus obtained has relatively high MW (above 40,000) and high viscosity (above 160,000 cP at 25°C). One way to obtain in DMSO a branched GAP product with relatively low MW (M_N ~ 5000) but with still a low VST value (i.e. below 0.7 ml/g), is to carry out the reaction at a higher temperature (such as 120°C) and choose a low cleaving agent concentration (cleaving agent /PECH below 0.030). As indicated in Table X, Sample N65 (VST = 0.4 ml/g, M_N = 6100) obtained at 120°C with a low ratio (cleaving agent/PECH) = 0.030 is relatively more stable than Sample E91 (VST = 2.0 ml/g, M_N = 5040) with a similar MW but synthesized at 100°C with a much higher concentration (cleaving agent /PECH) = 0.15. As shown in Table X, the polyol concentration used in the reaction had no significant effect on the VST results of the branched GAP samples synthesized in DMSO.

As indicated in Table XI, the thermal stability of the branched GAP samples prepared in DMA seems to vary with the polyol and cleaving agent concentrations used in the reaction. The samples (M_N = 4300-27,600) synthesized at 120°C with a ratio (polyol/PECH) below 0.50 and a ratio (cleaving agent/PECH) below 0.050 have VST values between 0.5 and 1.3 ml/g. On the other hand, the samples (M_N = 3600-17,600) obtained at 100-120°C with a ratio (polyol/PECH) = 0.5-1.0 and a ratio (cleaving agent/PECH) = 0.030-0.10 have VST values ranging from 0.7 to 3.5 ml/g. Consequently, branched GAP products with VST values below 2.0 ml/g can be obtained in DMA if low concentrations of polyol and cleaving agent are selected for the synthesis. In addition, if a stable product with relatively low MW (M_N ~ 5000) is desired, then the reaction should be conducted preferably at 120°C as was the case for GAP samples obtained in DMSO.

Therefore, the selection of a high reaction temperature (such as 120°C) and the use of low concentrations of cleaving agent and polyol (if DMA is chosen as solvent) enable the synthesis in DMSO and in DMA of second generation branched samples with a good thermal stability and with relatively low MW and viscosity. The branched GAP products thus obtained have VST values comparable with the measured value (VST = 0.40 ml/g) reported in Table XII for the commercial linear GAP diol (Ref. 21) supplied by Rockwell. As indicated in Table XII, the VST values of second generation branched GAP (prepared with specific reactants concentrations) are lower than the values found for first generation branched GAP (Ref. 22) and linear GAP (MW ~ 500) obtained by the single step process (Ref. 23). The synthesis method of these two GAP types involved the use of epichlorohydrin (ECH) and yielded unstable products with relatively high VST values (above 2.0 ml/g). The elimination of ECH in the degradation process enabled thus the production of second generation branched GAP with improved thermal stability.

3.5 Effect of Purification Procedure

3.5.1 Properties of Products Purified by the Extraction and Water Precipitation Techniques

The purification of second generation branched GAP according to the extraction and water precipitation techniques was described in Ref. 9. The properties of some GAP products synthesized in similar experimental conditions but purified by different procedures are presented in Table XIII for comparison purposes. All the GAP samples were obtained in DMSO after 32 h at 90°C with a ratio (CH_3OLi/PECH) = 0.075 and a ratio (glycerol/PECH) = 0.25-0.50. Samples N-06 and E150 were purified by extraction, whereas Sample N-07 was purified by water precipitation.

As shown in Table XIII, the values of M_N (3100), Me (990) and η (21,000 cP at 25°C) for Sample N-07 (purified by water precipitation) were about 16-57 % lower than the corresponding values found for the samples (N-06, E150) purified by extraction; however, all the samples had a similar value for f (3.1) indicating that the hydroxyl functionality was not affected by the purification procedure. On the other hand, the polymer yield for the water precipitation technique was about 85 % in comparison with a 95 % yield for the extraction procedure. Although all the samples listed in Table XIII are considered to be thermally stable (VST < 2 ml/g), nevertheless, the product purified by water precipitation has a lower VST value (1.2 ml/g) than the extraction products (VST = 1.7-1.8 ml/g).

Consequently the water precipitation technique gives products with enhanced thermal stability and with still an acceptable polymer yield. Besides, as reported in Ref. 9, the water precipitation technique does not require the large volumes of pollutant organic solvents (methanol, methylene chloride) and brine which are used in the extraction procedure. For all these reasons, the water precipitation technique is more cost-effective, environmentally friendly and very practical for large industrial scale compared with the extraction procedure which is more suitable for small laboratory scale. The water precipitation procedure has been chosen and applied by ICI Explosives Canada for the purification of second generation branched GAP at the McMasterville pilot plant.

3.5.2 Purification on Chromatographic Columns

The purification of some second generation branched GAP samples on chromatographic columns containing different adsorbents has been investigated and the results are presented in Table XIV. All the samples were obtained in DMSO after 16 h at 100°C with a ratio (CH_3OLi/PECH) = 0.10-0.15 and a ratio (glycerol/PECH) = 0.5-1.0.

Each GAP sample (20 g) was dissolved in 600 ml of methylene chloride ($MeCl_2$) and the resulting polymer solution was allowed to pass slowly (over a period of about 8 h) through a column filled with 10-25 g of adsorbents. Combinations of two or three of the following adsorbents were tested: silica gel, molecular sieve, activated charcoal, basic alumina. The first fraction (A) thus collected represented the GAP portion eluted with a non-polar solvent ($MeCl_2$). A second fraction (B) was obtained afterwards by passing a more polar solvent (mixture 700 ml methanol/300 ml $MeCl_2$) through the column over a period of approximately 8 h. The third fraction (C) corresponded to the GAP portion adsorbed on the column and was calculated by weight difference.

As shown in Table XIV, the polymer yield was 65-81 % for the first fraction (A) depending on the types of adsorbents used in the columns. The second fraction (B) eluted with a polar solvent represented 18-25 % of the polymer when silica gel was used in the column as observed for Samples E92 and E94; fraction (B) was much lower (3-5 %) for Samples E93 and E95 purified without using silica gel in the columns. The adsorbed fraction (C) corresponded to only 10-14 % of the polymer when silica gel or basic alumina were used in the columns as observed for Samples E92, E93 and E94. On the other hand, the amount of GAP which could not be recovered was much higher for Sample E95 (fraction C = 27 %) purified without silica gel or alumina.

The effects of the various adsorbents tested on the properties (M_N, Me, M_W/M_N, f, VST) of the collected GAP fractions are also presented in Table XIV. The values of Me and M_N determined for the first fractions (A) are higher than the corresponding values, measured for the original GAP samples, whereas the second fractions (B) have lower Me and M_N values compared with the original samples. This is an indication that fraction A (eluted with $MeCl_2$) has a lower hydroxyl content and a higher proportion of long polymeric chains than the original GAP sample and that fraction B (eluted with a more polar solvent) has more OH groups and a higher proportion of short chains compared to the original polymer. Fractions A and B have also generally higher values for the polydispersity index (M_W/M_N) and the hydroxyl functionality (f) compared with the original samples. As observed for Samples E92 and E95, the VST values measured for the fractions A (VST = 1.6-1.7 ml/g) are slightly lower than the values found for the original samples (VST = 2.0-2.2 ml/g).

This purification technique based on adsorption chromatography is not cost-effective since it requires large solvent volumes (80 ml/g polymer) and large amounts of adsorbents (1 g/g polymer) as well as long time period (1 h /g polymer). Besides, the collected fractions have different characteristics (MW, hydroxyl functionality etc.) compared with the original sample and the polymer yield for the combined fractions (A and B) varies betwen 73 % and 90 %, depending on the adsorbents used in the column.

Since second generation branched GAP products synthesized in DMSO or DMA by selecting some specific reaction parameters and purified by the extraction or water precipitation procedures, had VST values below 1.3 g/ml (as indicated in Subsections 3.4.4 and 3.5.1). Therefore, there is no real advantage to apply the adsorption technique for purification purposes in order to improve the thermal stability of the product.

3.6 Effect of Stabilizers and Additives

3.6.1 Effect of Stabilizers Added in the Final Product

The effects of stabilizers on the thermal stability of second generation branched GAP are presented in Table XV. Three different stabilizers were tested: DBHQ (di-ter-butyl hydroquinone), Santonox [4,4'-thio-bis(6 ter-butyl-m-cresol)] and potassium pyroantimoniate. In each case, the stabilizer was added in a concentration of 16 % to the final product after the purification stage. The stabilizer was used in excess at relatively high concentration in order to emphasize its effect on the polymer thermal stability. All the VST experiments were carried out with the same GAP sample (N117) in order to assess and compare the effects of the different stabilizers. Sample N117 was obtained in DMSO after 16 h at 120°C using CH_3OLi as cleaving agent and hexanetriol as polyol.

As shown in Table XV, the VST value was first determined for Sample N117 without stabilizer and then for the GAP sample containing each of the three stabilizers investigated. The addition of DBHQ had no significant effect on the thermal stability of the final product since the measured VST value (2.7 ml/g) was practically similar to the value obtained for the original GAP sample (VST = 2.5 ml/g) tested without stabilizer. On the other hand, the thermal stability of GAP was enhanced with Santonox since the VST value was reduced to 1.9 ml/g. The addition of potassium pyroantimoniate greatly improved the thermal stability of the branched GAP product which had a VST value of 0.8 ml/g.

As mentioned in Subsection 3.4.4, second generation branched GAP with a VST value below 1.3 ml/g can be obtained just by selecting some specific synthesis parameters and even without using any additive. Therefore, the addition of stabilizers to the final product should be considered mainly to improve the long-term stability of branched GAP during storage. This topic as well as the choice of the most convenient stabilizer and its optimum concentration require further investigation.

3.6.2 Effects of Stabilizers Included in the Synthesis Reaction

The effects of different stabilizers (included in the synthesis reaction) on the properties (M_w, VST) of the branched GAP product are presented in Table XVI. The GAP samples were prepared in DMSO for 16 h at 120°C. Various stabilizers were investigated: DBHQ, Santonox, Quinol (hydroquinone) and Triphenyl Phosphine (TP).

The GAP samples listed in Table XVI are separated into three groups. The first group comprises the samples (N115, E203, E198, E197) prepared without polyol, whereas the second group represents the samples (N75, E201, E199, E200) synthesized using TMP as polyol with a ratio (TMP/PECH) = 0.25. All the GAP samples in the first and second groups were prepared with a ratio (CH_3OLi/PECH) = 0.030; a ratio (stabilizer/PECH) = 0.025 was used for these polymers except for the reference samples (N115, N75) that were synthesized without stabilizer. The samples in the third group were obtained without cleaving agent and using a constant ratio (TMP/PECH) = 0.25 but with a variable concentration of stabilizer (TP).

The results obtained for the samples in the first and second groups indicate that the addition of stabilizers to the reaction mixture yielded products with MW higher than the polymers prepared without stabilizers. The MW increase was more significant for the stabilizers containing hydroxyl groups (Santonox, DBHQ, Quinol) than for a stabilizer without hydroxyl group such as TP. When TMP was included as polyol in the synthesis of the samples in the second group, the MW increase caused by the addition of stabilizers, was less significant in comparison with the samples of the first group obtained without polyol. Consequently, the stabilizers included in the reaction with a ratio (stabilizer/PECH) = 0.025, hinder the degradation mechanism. The GAP products thus obtained have a relatively higher MW compared with the reference samples synthesized without stabilizers. Besides, gelling occurred for the products with M_w exceeding 20,000 as observed for Samples E197, E198 and E200. For these products, additional solvent was required to dissipate the gel formed during the synthesis. Sample E206 (M_w = 120,000) of the third group which was obtained with a relatively low stabilizer concentration (TP/PECH = 0.025) has also a higher MW in comparison with the reference sample N94 (M_w = 96,200) prepared without stabilizer. As the concentration of stabilizer is increased furthermore, a reverse phenomenon occurs and produces the opposite effect: a MW decrease. This phenomenon was observed in the third group for Samples E207 (M_w = 46,200) and E 208 (M_w = 19,100) prepared respectively with a ratio (TP/PECH) of 0.050 and 0.10. This is an indication that at high concentration, TP behaves as a cleaving agent by promoting the scission of polymeric chains. Therefore, the stabilizer included in the synthesis participates in the reaction mechanism and, depending on its concentration, can either produce a MW increase via chain extension (or cross-linking) or a MW decrease via chain scission.

P154755.PDF [Page: 26 of 66]

As shown in Table XVI, the VST values of the GAP samples prepared with stabilizers are either similar or higher than the values determined for their corresponding reference samples. Therefore, the addition of stabilizers in the synthesis reaction did not improve the thermal stability of the branched GAP product. Since the stabilizers included in the synthesis interfere with the degradation mechanism without enhancing the stability of the product, therefore there is no advantage to add stabilizers to the reaction mixture.

3.6.3 Effects of Lithium Compounds Additives

The effects of some Lithium compounds additives on the properties (M_w, VST) of the branched GAP product are presented in Table XVII. All the GAP samples were obtained in DMSO after 16 h at 120°C using CH_3ONa as cleaving agent and TMP as polyol with a ratio (TMP/PECH) = 0.25. The lithium salts investigated are lithium chloride (LiCl), lithium sulfide (Li_2S) and lithium tetraborate. These compounds were included in the reaction mixture before the addition of NaN_3 and CH_3ONa. As reported in Ref. 9, CH_3ONa was less effective than CH_3OLi in terms of chain cleavage and MW reduction. On the other hand, CH_3ONa is relatively cheap and is therefore more cost-effective than CH_3OLi, especially when used at large industrial scale. The purpose of these experiments was thus to find out whether the addition of lithium salts to the reaction mixture and the resulting lithium ions effects could increase the reactivity of CH_3ONa and enhance its chain scission efficiency.

As shown in Table XVII, Sample N119 (M_w = 38,000) obtained by adding LiCl in a ratio (LiCl/PECH) = 0.25 has a MW lower than reference sample E210 (M_w = 47,000) prepared with a similar ratio (CH_3ONa/PECH) = 0.03 but without LiCl. Therefore, at a relatively low cleaving agent concentration (CH_3ONa/PECH = 0.03), the addition of LiCl to the reaction mixture caused a slight reduction in the MW of the GAP product. However, at higher cleaving agent concentration, the addition of LiCl caused the opposite effect: a MW increase. Samples N121 (M_w = 30,500) and N122 (M_w = 510,000) synthesized respectively with a ratio (LiCl/PECH) of 0.25 and 0.75 had relatively higher MW compared with the reference sample E211 (M_w = 19,000) obtained with a similar ratio (CH_3ONa/PECH) = 0.050 but without LiCl. Besides the MW increase was proportional to the amount of LiCl added to the reaction mixture. Samples E209 (M_w = 70,000) obtained with a ratio (Li_2S/PECH) = 0.015 and E212 (M_w = 51,800) prepared with a ratio (Li tetraborate/PECH) = 0.030 had also relatively higher MW compared with the reference sample E210 (M_w = 47,000) synthesized with a similar cleaving agent concentration (CH_3ONa/PECH = 0.030) but without lithium additive. Therefore, the addition of Li_2S and lithium tetraborate even in relatively low proportions caused nevertheless a MW increase for the GAP product.

Consequently, the addition of lithium compounds to the reaction mixture did not increase the chain cleavage efficiency of CH_3ONa to the level attained by CH_3OLi. In most cases, the lithium additives rather reduced the reactivity of CH_3ONa and hindered the degradation mechanism.

As shown in Table XVII, the VST values of the GAP samples obtained with lithium compounds are either similar or higher than the values measured for their corresponding reference samples synthesized without additives. Therefore, the addition of lithium salts in the synthesis reaction did not improve the thermal stability of the branched GAP product. Since the lithium compounds included in the synthesis did not enhance neither the chain scission efficiency of CH_3ONa nor the stability of the product. Therefore, there is no advantage to add lithium salts to the reaction mixture.

4.0 CONCLUSIONS

The hydroxyl functionality, the equivalent weight and the MW polydispersity of second generation branched GAP increase with the MW of the product. The degree of branching and the average number of OH groups per molecule increase with the polymer chain length. The GAP products obtained in DMSO, DMA and DMF have the same viscosity-MW and functionality-MW relationships.

The branched GAP samples synthesized without using any polyol in the reaction have a different distribution of hydroxyl functionality than those obtained from reactions involving polyols. The addition of a polyol into the reaction mixture enhances the reactivity of the cleaving agent and causes a further reduction in the MW and viscosity of the GAP produc. Additional OH groups (originating from the polyol) are thus incorporated into the GAP molecular structure.

Branched GAP prepared without cleaving agent has relatively higher MW (40,000-200,000) and hydroxyl functionality (above 10) compared with the GAP product (MW < 40,000 and f < 10) of a reaction involving a basic cleaving agent.

Second generation branched GAP has a Tg value of -46 ± 5°C; the product with a high degree of branching seems to have a slightly lower Tg value than the polymer with a lower functionality and MW.

The branched GAP samples prepared with CH_3OLi had generally higher heats of formation (ΔH_f = 37.5 ± 17 % kcal/mole) compared with the samples synthesized with NaOH (ΔH_f = 29.9 ± 13 % kcal/mole). The reaction parameters had no significant effect on the heat of decomposition (ΔH_d = 490 ± 15 % cal/g).

P154755.PDF [Page: 28 of 66]

The TGA thermogram of branched GAP consists of a two-stage or one-stage weight loss process which seems to depend on the amount of sample tested.

The purification of branched GAP by the water precipitation technique gives products with enhanced thermal stability and with still an acceptable polymer yield (85%). The extraction procedure gives a better polymer yield (95 %), but is not convenient for large industrial scale since it requires large volumes of organic solvents and brine.

The purification of branched GAP on chromatographic columns is not cost-effective since it requires large solvent volumes and amounts of adsorbents and lasts long time periods. Besides this adsorption technique alters the properties of the product without improving significantly its thermal stability.

There is no advantage to add a stabilizer to the reaction mixture because the stabilizer included in the synthesis participates and interferes with the degradation mechanism without enhancing the thermal stability of the GAP product. On the other hand, the addition of a stabilizer to the final product (after the purification stage) should be considered mainly to improve the long term stability of branched GAP during storage.

The addition of lithium compounds to the reaction mixture did not increase the chain cleavage efficiency of CH_3ONa to the level attained by CH_3OLi. In most cases, the lithium additives had the opposite effect and hindered the degradation mechanism.

Second generation branched GAP with a good thermal stability and with relatively low MW and viscosity can be prepared in DMSO or DMA by selecting some specific synthesis parameters. A GAP product with a low VST value (below 0.7 ml/g) and low MW (M_N = 5000) is thus obtained in DMSO by choosing a low cleaving agent concentration (CH_3OLi/PECH below 0.030) and conducting the reaction at 120°C. Branched GAP with high viscosity and MW, obtained without including any cleaving agent in the synthesis reaction, can be used in the preparation of energetic thermoplastic elastomers.

5.0 ACKNOWLEDGEMENTS

The author would like to express his sincere thanks to Mr. J. Angers and Mrs. N. Gagnon for their valuable technical assistance and contribution. Special thanks are also addressed to the members of the "Branched GAP Project Team" at DREV and to the representatives of ICI Explosives Canada involved in the DIR project for many useful discussions over the last few years.

P154755.PDF [Page: 29 of 66]

6.0 REFERENCES

1. Ahad, E., "Branched Energetic Polyether Elastomers",
- U.S. Pat. 5,130,381, 14 July 92
- U.S. Pat. 5,191,034, 02 Mar 93
- Can. Pat. Appl. 2,061,744-6, filed 24 Feb 92
- PCT International Appl. No. PCT/CA92/00144, filed 03 Apr 92
- Europ. Pat. Appl. No. 92907672-7, DE, FR, GB, NL, 03 April 92.

2. Ahad, E., "Improved Branched Energetic Azido Polymers", U.S. Pat. Appl. 08/130,129, filed 04 oct 93.

3. Ahad, E., "A Novel Degradation Process for the Synthesis of Branched GAP", Proceedings of the 18th Meeting TTCP (W4), Fort Halstead, UK, Apr 93.

4. Ahad, E., Lessard, P., Lavigne, J., Thiboutot, S., Villeneuve, S., Dubois, C., Druet, L., Désilets, S., Lavertu, R., Twardawa, P., Barna, J.A., Dewyse, V., Gray, G., Groeneweg, P., Holden, W. and Witwit, S., "Branched GAP: Properties, Pilot-Plant and Applications", Proceedings of the 24th International Annual Conference of ICT, "Energetic Materials - Insensitivity and Environmental Awareness", 29 June-02 July 93, Karlsruhe, Germany.

5. Holden, H.W., "Glycidyl Azide Polymer - An Advanced Binder", ICI Explosives Canada, Final Report No. MTC-93/11-23F (Cat. B), DIRP Agreement 22079-EV03, 25 Nov 93.

6. Gray, G. and Kilcullen, D., "The Chemistry of Glycidyl Azide Polymer", ICI Explosives Canada, MTC-94/01-01F (Cat. B), 12 Jan 94.

7. Barna, J.A., Groeneweg, P.G., Holden, H.W. and Leonard, J.A., "Pilot Plant for Azido Polymers: Branched GAP Process and Properties", ADPA International Symposium on Energetic Materials Technology, March 94, Orlando, Florida, U.S.A.

8. Dubois, C. and Roy, A., "Bench-Scale Production of Branched Glycidyl Azide Polymer: An Alternate Route to Final Product", DREV - R-9415, June 1995, UNCLASSIFIED

9. Ahad, E., "Improved Process for the Synthesis of Second Generation Branched GAP", DREV - R-9414, April 1995, UNCLASSIFIED

P154755.PDF [Page: 30 of 66]

10. Annual Book of ASTM Standards for Bomb Calorimetry and Combustion Methods, D240-76 (Reapproved 1980).

11. Standardization Agreement, STANAG No. 4147, AC/310-D/15, "Chemical Compatibility of Ammunition Components with Explosives and Propellants (Non Nuclear Application), NATO, UNCLASSIFIED.

12. MIL-STD-650, Method 503.1, "100°C and 120°C Vacuum Stability Test", 3 August 1962.

13. Malotky, L. and Heller, H., "Vacuum Stability Test", J. Hazardous Mat., Vol. 2, pp. 189-195, 1977.

14. Simmons, Jr., H.T., "The Vacuum Thermal Stability Test for Explosives", NOLTR 70-142, Naval Surface Weapon Center, White Oak, MD, 28 October 1970.

15. Lavigne, J., Lessard, P., Ahad, E. and Dubois, C., "Correlation of Propellant Mechanical Properties and Branched GAP Synthesis Parameters", ADPA International Symposium on Energetic Materials Technology, March 1994, Orlando, Florida, U.S.A.

16. Lessard, P., Ahad, E., Lavigne, J. and Dubois, C., "Branched GAP/AN Propellant: Effect of Polyol Co-Reagent on Mechanical Properties", Proceedings of the 19th Meeting TTCP (W4), DREV, Québec, Canada, May 1994.

17. Ahad, E., Lavigne, J., Lessard, P. and Dubois, C., "Effect of Branched GAP Synthesis Parameters on Mechanical Properties of Rocket Propellants", DREV - R-9513, UNCLASSIFIED

18. Ahad, E., "Azido Thermoplastic Elastomers", U.S. Pat. 5,223,056, 29 June 93.

19. Kubota, N. and Sonobe, T., "Combustion Mechanism of Azide Polymer", J. Prop., Expl, Pyro., 13, 172-177, 1988.

20. Lavigne, J., Ahad, E., Désilets, S., Thiboutot, S., Lussier, L.-S., Ampleman, G. et Lee, A.K., "Caractérisation chimique d'un polyazoture de glycidyle à structure ramifiée", CRDV M-3055/91, novembre 1991, SANS CLASSIFICATION

21. Frankel, M.B., Grant, L.R. and Flanagan, J.E., "Historical Development of GAP", J. Propulsion & Power, Vol. 8, No. 3, p. 560-563, May-June 92.

P154755.PDF [Page: 31 of 66]

22. Ahad, E., "Synthesis and Characterization of Branched Glycidyl Azide Polymer", DREV - R-4634/91, May 1991, UNCLASSIFIED

23. Ahad, E., "Single-Step Synthesis of Glycidyl Azide Polymer", DREV - R-4544/89, March 1989, UNCLASSIFIED

P154755.PDF [Page: 33 of 66]

TABLE I

Solution properties of branched GAP synthesized in DMSO

Sample	$[\eta]_{THF}$ dl/g	M_w	M_N	$\left(\frac{M_w}{M_N}\right)$	Me	f	η25°C cP
N103-2	0.48	168,000	48,000	3.5	3800	12.6	2.8×10^6
N94-2	0.34	100,000	35,000	2.9	3500	10.0	1.0×10^6
E110	0.26	57,000	22,800	2.5	3200	7.1	400,000
N97	0.19	35,000	15,200	2.3	2900	5.2	128,000
E149	0.15	25,000	11,400	2.2	2600	4.4	100,000
N88	0.11	17,000	8500	2.0	2300	3.7	60,000
E150	0.095	13,000	6500	2.0	2000	3.2	50,000
E147	0.084	10,000	5000	2.0	1700	2.9	41,000
E145	0.073	8000	4200	1.9	1550	2.7	31,000
E143	0.062	6000	3200	1.9	1280	2.5	28,000
E141	0.050	4000	2200	1.8	960	2.3	22,000
E238	0.040	2600	1400	1.8	600	2.3	16,000

TABLE II

Solution properties of branched GAP synthesized in DMA

Sample	$[\eta]_{THF}$ dl/g	M_w	M_N	$\left(\frac{M_w}{M_N}\right)$	Me	f	$\eta_{25°C}$ cP
E163	0.28	68,000	27,000	2.5	3300	8.3	482,000
E164	0.24	54,000	22,500	2.4	3200	7.0	342,000
E161	0.17	32,000	13,900	2.3	2900	4.8	95,000
N35	0.13	21,000	9500	2.2	2500	3.8	76,000
N21	0.10	16,000	7600	2.1	2200	3.5	64,000
N41	0.090	12,000	6000	2.0	1900	3.1	45,000
N43	0.080	9000	4700	1.9	1650	2.8	38,000
N46	0.070	7500	4200	1.8	1500	2.8	35,000
N42	0.063	6200	3400	1.8	1300	2.6	30,000

TABLE III

Solution properties of branched GAP synthesized in DMF

Sample	$[\eta]_{DMF}$ dl/g	M_w	M_n	$\left(\frac{M_w}{M_N}\right)$	Me	f	η25°C cP
E170	0.33	98,000	42,600	2.3	3700	11.5	1.8×10^6
E168	0.27	62,000	28,200	2.2	3400	8.3	516,000
E167	0.23	45,000	21,400	2.1	3100	6.9	287,000
E166	0.20	36,000	18,000	2.0	2950	6.1	147,000
E245	0.12	18,000	9000	2.0	2400	3.8	58,000
E171	0.088	11,000	5800	1.9	1850	3.1	38,000
E169	0.075	8500	4700	1.8	1650	2.8	34,000

TABLE IV

Properties of branched GAP synthesized without polyol

Sample*	$\left(\frac{CH_3OLi}{PECH}\right)$	M_w	Me	f	$\eta_{25°C}$ cP
E251	0.0125	43,500	2955	5.4	182,000
E252	0.0137	34,600	2680	5.2	131,000
E194	0.0150	28,000	2575	5.1	104,000
N115	0.030	12,100	1660	2.8	47,000
E195	0.040	7800	1310	2.6	40,000

* All GAP samples were obtained in DMSO after 16 h at 120°C

TABLE V

Comparison of properties of branched GAP synthesized with and without polyol

Properties — Sample*		N75 (with TMP)	N95 (without Polyol)
M_w		9500	12,800
M_n		5000	5800
(M_w/M_n)		1.9	2.2
Me		1360	1810
$f = (M_n/Me)$		3.7	3.2
η25°C (cP)		42,000	54,000
functionality distribution	above 3.5	38.4 %	51.5 %
	2 - 3.5	59.3 %	46.3 %
	below 2	2.3 %	2.2 %

* Both GAP samples were obtained in DMSO after 16 h at 120°C with $(CH_3OLi/PECH) = 0.030$

Sample N75 was synthesized using TMP as polyol with a weight ratio (TMP/PECH) = 0.25

TABLE VI

Properties of branched GAP synthesized without cleaving agent

Sample*	Polyol	$\left(\frac{\text{Polyol}}{\text{PECH}}\right)$	Reaction		M_w	Mc	f	$\eta_{25°C}$ cP
			Temperature °C	time (h)				
N113	NONE	0	120	16	103,500	3600	11.4	1.48×10^4
N94	TMP	0.25	120	16	96,200	3500	11.5	7.8×10^3
N96	PE	"	"	"	85,200	3400	10.6	6.9×10^3
N103	TMP	0.25	100	32	174,000	3800	15.6	2.6×10^4

* All GAP samples were obtained in DMSO

TABLE VII

Glass transition temperature of branched GAP

Sample*	Synthesis Parameter		M_w	f	Tg (°C)
	Solvent	Polyol			
Linear	-	-	2250	1.5	-45
E108	DMA	Glycerol	9700	3.0	-42
E46		EG	25,000	4.7	-47
E112		PEG (MW 600)	81,000	11.2	-48
N98	DMSO	PE	8950	3.0	-41
N107		PE (60%)/HT(40%)	9250	3.1	-42
N75		TMP	9500	3.7	-41
N111		PE(60%)/PEG 600 (40%)	9870	3.4	-43
N112		TMP(60%)/PEG 600(40%)	10,300	3.3	-44
N110		PEG (MW 600)	11,600	2.8	-46
N95		NONE	12,800	3.2	-43
E118		PEG (MW 400)	17,300	3.8	-47
E107		Glycerol	33,000	5.6	-49
E261		NONE	74,700	6.4	-51

* All branched GAP samples were prepared using CH_3OLi as cleaving agent

The linear GAP sample is a diol (lot 1000-10-2) obtained from 3M Company

TABLE VIII

Heats of combustion and formation of branched GAP

Sample	Synthesis Parameter			- ΔH_c ± 15 cal/g	- ΔH_f ± 1.5 Kcal/mole
	Solvent	Polyol	Cleaving Agent		
E59	DMA	Glycerol	NaOH	4851	27.5
E58		"		4870	29.4
E54		"		4884	30.8
E62		"		4900	32.3
E97		EG	CH_3OLi	4905	32.8
E108		EG		4993	41.6
E77		Glycerol		5001	42.3
E89	DMSO	Glycerol	CH_3OLi	4931	35.4
E102-3		"		4945	36.8
E91		"		4960	38.3
E98-9		"		4974	39.7
E88		"		5000	42.3

TABLE IX

Heat of decomposition of branched GAP

Sample*	Polyol	Reaction			Tp °C	Δ H_d cal/g
		Solvent	Temperature °C	time (h)		
linear GAP	-	-	-	-	254	523
E33	EG	DMA	100	32	254	553
E37	"	"	"	"	255	457
E38	"	"	"	"	253	562
N116	HT	DMSO	120	16	253	415
N98	PE	"	"	"	253	472
N115	NONE	"	"	"	251	557

* All branched GAP samples were synthesized with CH_3OLi as cleaving agent

The linear GAP is lot 1000-10-2 obtained from 3M Company

TABLE X

Thermal stability of branched GAP synthesized in DMSO

Sample	Reaction Temperature °C	$\left(\frac{\text{CleavingAgent}}{\text{PECH}}\right)$	$\left(\frac{\text{Polyol}}{\text{PECH}}\right)$	M_n	VST ml/g
E144	90	0.10	1.0	2300	1.6
E155		0.10	0.5	2300	1.6
E150		0.075	0.25	4250	1.8
E91	100	0.15	0.5	5040	2.0
E133		0.10	1.0	3000	1.7
E122		0.10	0.5	4400	2.0
E152	120	0.050	1.0	3600	1.8
N66		0.045	1.0	6200	1.2
N69		"	0.25	16.600	0.8
N71		"	0.15	4000	1.4
E148		0.040	0.25	6750	1.1
E149		"	0.25	6940	0.9
E195		"	0	3700	1.1
N12		0.032	1.0	4900	1.0
E159		0.030	1.0	3600	0.5
N11		"	"	4600	0.6
N16		"	"	6000	0.6
E216		"	"	7600	0.4
N65		"	0.25	6100	0.6
N78		"	0.20	4265	0.7
N95		"	0	5800	0.6
N13		0.025	1.0	7560	0.6
N105		0.020	0.25	7500	0.5
N89		"	0.15	6400	0.5
N88		"	0.025	7800	0.3
E194		0.015	0	13,500	0.4
E252		0.013	0	13,600	0.6
N96		0	0.25	36,100	0.4

TABLE XI

Thermal stability of branched GAP synthesized in DMA

Sample	Reaction Temperature °C	$\left(\frac{\text{Cleaving Agent}}{\text{PECH}}\right)$	$\left(\frac{\text{Polyol}}{\text{PECH}}\right)$	M_n	VST ml/g
E97	100	0.10	1.0	4300	2.8
E125		"	"	4900	2.9
E124		"	"	11,200	2.9
N28	120	0.050	1.0	4990	2.2
E162		"	"	7740	2.2
N30		"	"	5830	1.3
N48		"	"	8770	1.1
N43		"	0.25	5300	1.3
N47		"	"	8300	1.3
N45		"	"	11,950	0.7
N42		"	"	3600	0.7
N44		"	"	8000	0.6
N46		"	"	4800	0.5
E172		0.045	1.0	5500	1.7
N29		"	"	6000	1.4
N49		"	"	11,400	0.9
E176		"	0.50	10,900	0.7
N76		"	0.25	6700	0.5
N32		"	"	6700	0.8
N34		"	"	9500	0.8
N36		"	"	9900	0.6
N35		"	"	10,700	0.5
N37		"	"	28,000	0.6
N27		0.040	1.0	6800	2.2
N26		"	"	8300	1.9
N24		"	"	6600	1.6
N21		"	"	8300	0.7
E163		"	0.25	27,600	0.5
E161		0.030	1.0	17,600	3.5
E258		"	1.0	11,400	3.2
N57		"	0.5	7000	0.7
E257		"	0	16,300	0.9

TABLE XII

Thermal stability of different types of GAP

GAP			Synthesis			VST
Source	Structure	MW	nb of steps	Process	Reference	ml/g
Rockwell	linear	2000	2	A	21	0.4
DREV	linear	500	1	B	23	above 2
DREV	Branched (1st generation)	500-40,000	1	C	22	above 2
DREV	Branched (2nd generation)	1000-200,000	1	D	9	0.3-0.7 (DMSO) 0.5-1.3 (DMA)

Process. A: Polymerization and azidation accomplished separately in two distinct steps

B: Polymerization and azidation achieved simultaneously by direct conversion of epichlorohydrin (ECH) to GAP

C: Degradation and azidation of rubbery PECH and ECH

D: Degradation and azidation of rubbery PECH without ECH
DMSO: (cleaving agent/PECH) = 0-0.030
DMA: (polyol/PECH) = 0-0.50
(cleaving agent/PECH) = 0-0.050

TABLE XIII

Properties of branched GAP products purified by the extraction and water precipitation procedures

Purification Procedure	Sample*	M_n	Me	η25°C cP	f	Polymer Yield %	VST m²/g
Extraction	N-06	3600	1218	27,000	3.0	95	1.7
	E150	4200	1360	33,000	3.1	95	1.8
Water Precipitation	N-07	3100	990	21,000	3.1	85	1.2

* All GAP samples were obtained in DMSO after 32 h at 90°C with (CH_3OLi/PECH) = 0.075 and (glycerol/PECH) = 0.25-0.50

TABLE XIV

Purification of branched GAP on chromatographic columns

Adsorbents	GAP		Polymer Yield %	Mn	Mw	$\left(\frac{M_w}{M_n}\right)$	f	VST ml/g
	Sample	Fraction						
I	E92	original		750	1725	1.8	2.3	2.2
		A	70	894	3000	2.3	3.4	1.6
		B	18	478	1245	2.4	2.6	
		C	12					
II	E93	original		800	1800	1.8	2.3	
		A	81	900	3560	2.2	3.9	
		B	5	485	1455	2.3	3.0	
		C	14					
III	E94	original		950	2200	1.8	2.3	
		A	65	1280	4020	2.0	3.1	
		B	25	647	1815	2.2	2.8	
		C	10					
IV	E95	original		800	1800	1.8	2.3	2.0
		A	70	852	2356	2.4	2.8	1.7
		B	3	491	1280	2.5	2.6	
		C	27					

All GAP samples were obtained in DMSO after 16 h at 100°C
with (CH_3OLi/PECH) = 0.10-0.15 and (glycerol/PECH) = 0.50-1.0

Adsorbents used for 20 g GAP:

	activated charcoal	/ silica gel	/ Molecular Sieve	/ basic alumina
I :	5 g	10 g	5 g	0
II :	5	0	5	10 g
III :	0	20	5	0
IV :	20	0	5	0

Fraction A : eluted with $MeC\ell_2$
B : eluted with 70% methanol/30% $MeC\ell_2$
C : adsorbed on column

P154755.PDF [Page: 47 of 66]

TABLE XV

Effect of stabilizers added in the final branched GAP product

Sample	VST mℓ/g
N117 (without stabilizer)	2.5
N117 + DBHQ (16%)	2.7
N117 + Santonox (16%)	1.9
N117 + K Pyroantimoniate (16%)	0.8

Sample N117 was synthesized in DMSO for 16 h at 120°C with CH_3OLi as cleaving agent and hexanetriol as polyol

TABLE XVI

Effect of stabilizers included in the synthesis reaction

Sample*	Stabilizer	Stabilizer / PECH	Polyol	Polyol / PECH	CH_3OLi / PECH	M_w	VST ml/g
N115	NONE	0	NONE	0	0.030	12,115	1.5
E203	TP	0.025	"	0	"	15,700	2.1
+E198	DBHQ	0.025	"	0	"	21,300	1.4
+E197	Santonox	0.025	"	0	"	24,900	1.4
N75	NONE	0	TMP	0.25	0.03	9500	0.8
E201	TP	0.025	"	"	"	10,800	1.7
E199	Santonox	0.025	"	"	"	15,400	2.1
+E200	Quinol	0.025	"	"	"	23,800	0.8
N94	NONE	0	TMP	0.25	0	96,200	1.0
E206	TP	0.025	"	"	0	120,000	1.0
E207	TP	0.05	"	"	0	46,200	
E208	TP	0.10	"	"	0	19,100	

* All GAP samples were obtained in DMSO after 16 h at 120°C

\+ Gelling occured and additional solvent was required

TABLE XVII

Effect of lithium compounds additives on the properties of the GAP product

Sample*	Additive	Additive / PECH	CH_3ONa / PECH	M_w	VST (ml/g)
E210	NONE	0	0.03	47,000	1.3
E211	"	0	0.05	19,000	2.2
N119	LiCl	0.25	0.03	38,000	1.0
N121	"	0.25	0.05	30,300	2.0
N122	"	0.75	0.05	510,000	
E209	Li_2S	0.015	0.03	70,000	5.0
E212	Li Tetraborate	0.030	0.03	51,800	1.1

* All the GAP samples were obtained in DMSO after 16 h at 120°C with (TMP/PECH) = 0.25

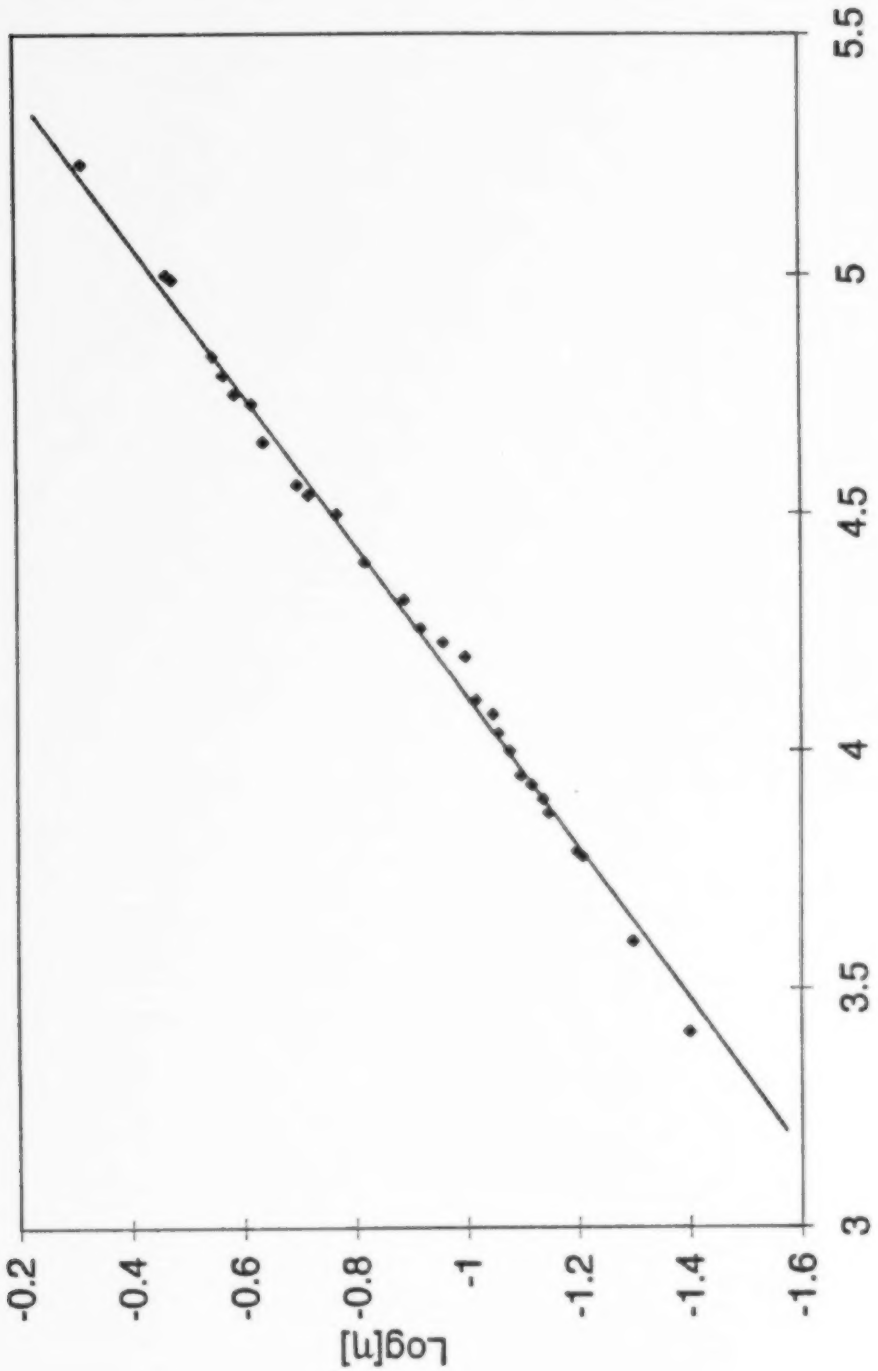

FIGURE 1 - Intrinsic viscosity-molecular weight relationship for branched GAP

P154755.PDF [Page: 52 of 66]

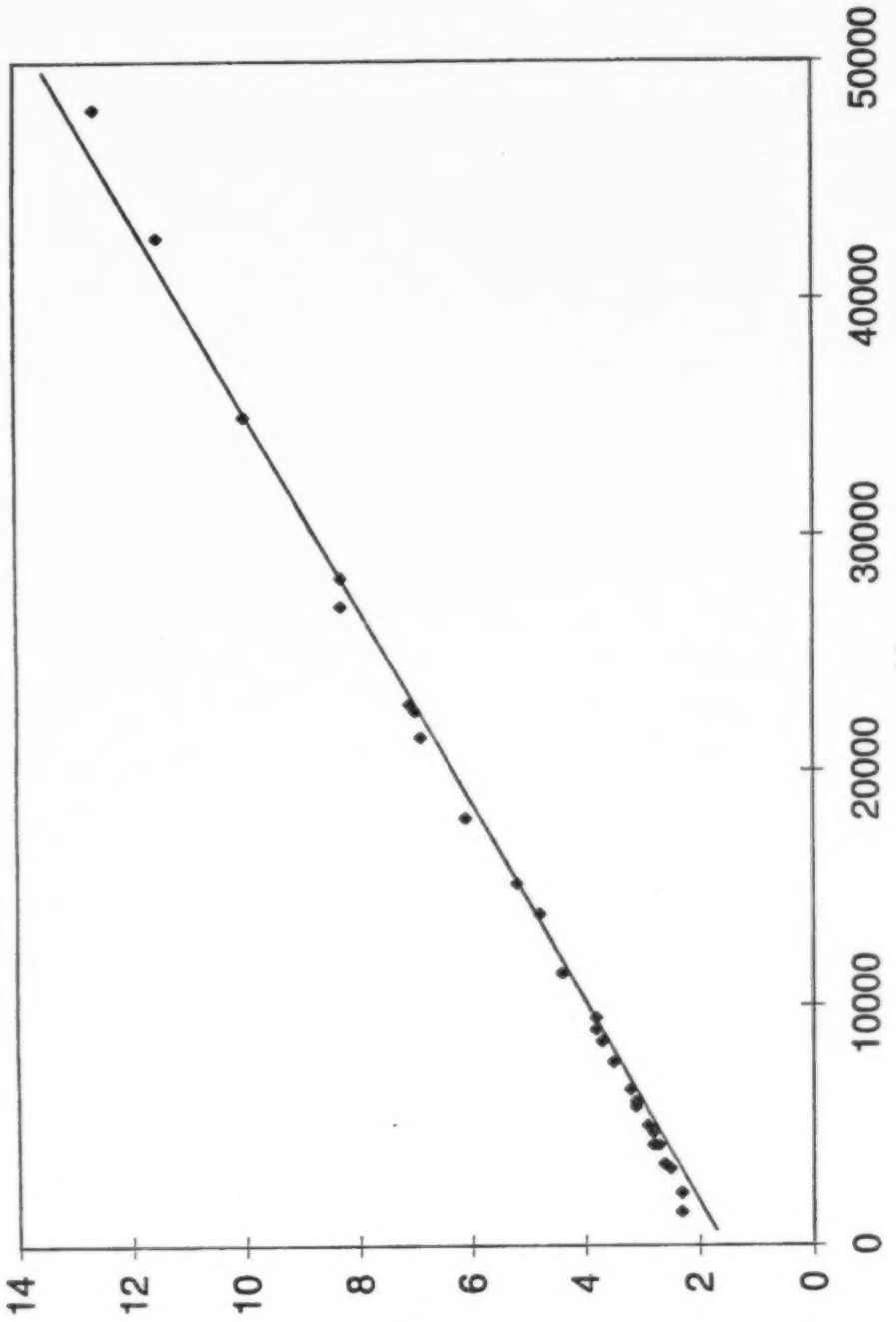

FIGURE 2 - Functionality-molecular weight relationship for branched GAP

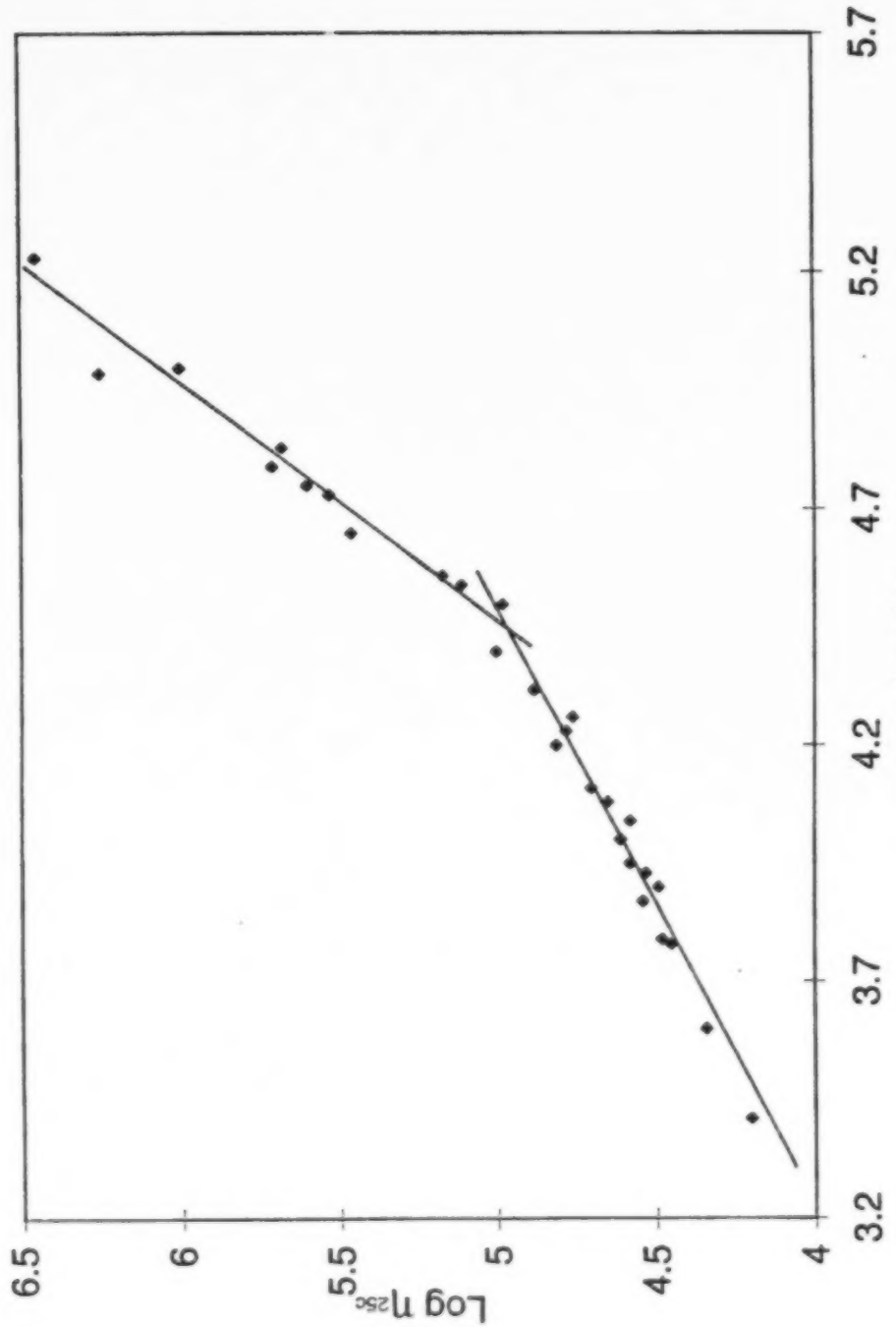

FIGURE 3 - Absolute viscosity-molecular weight relationship for branched GAP

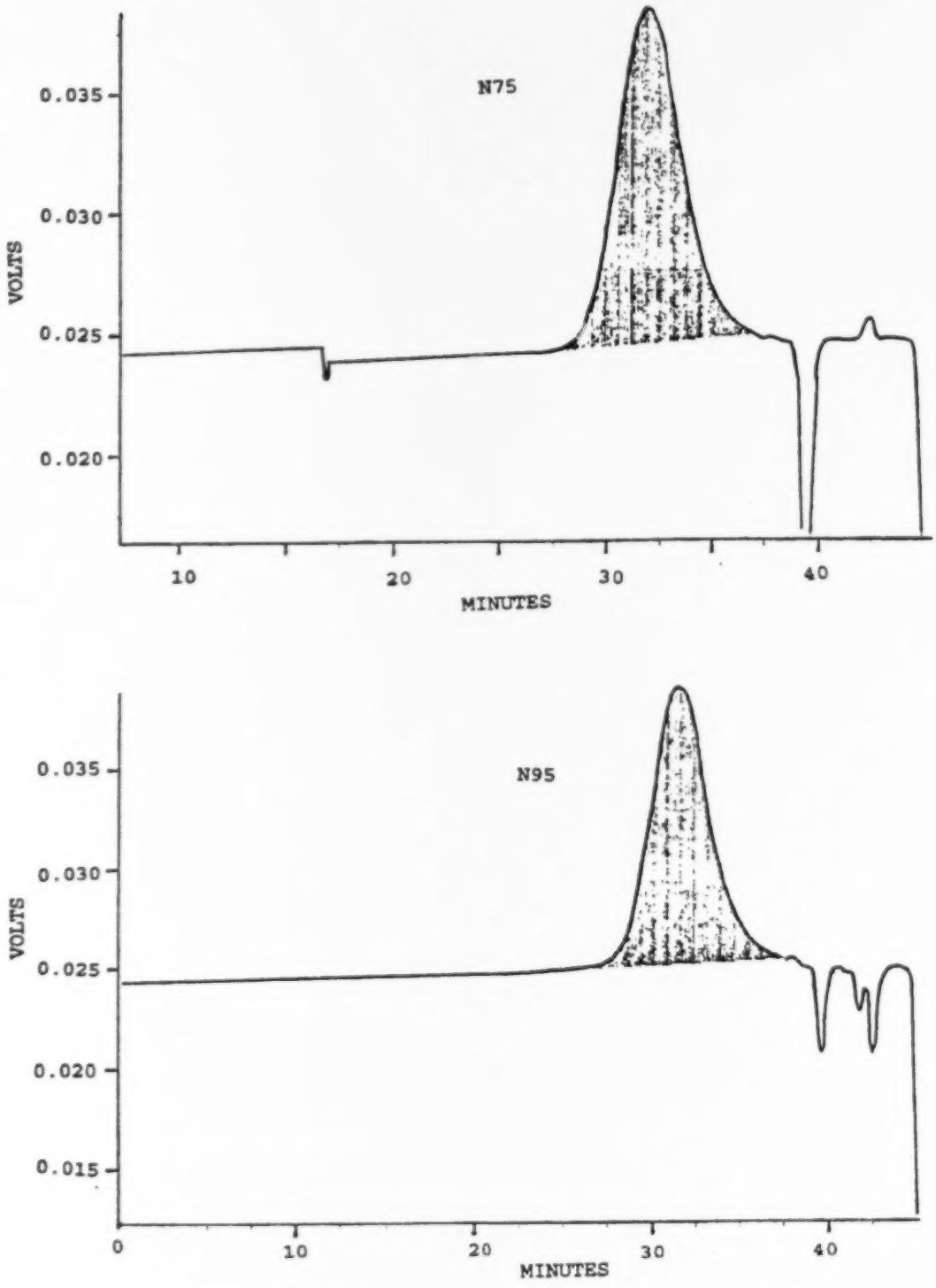

FIGURE 4 - GPC chromatograms of Samples N75 and N95

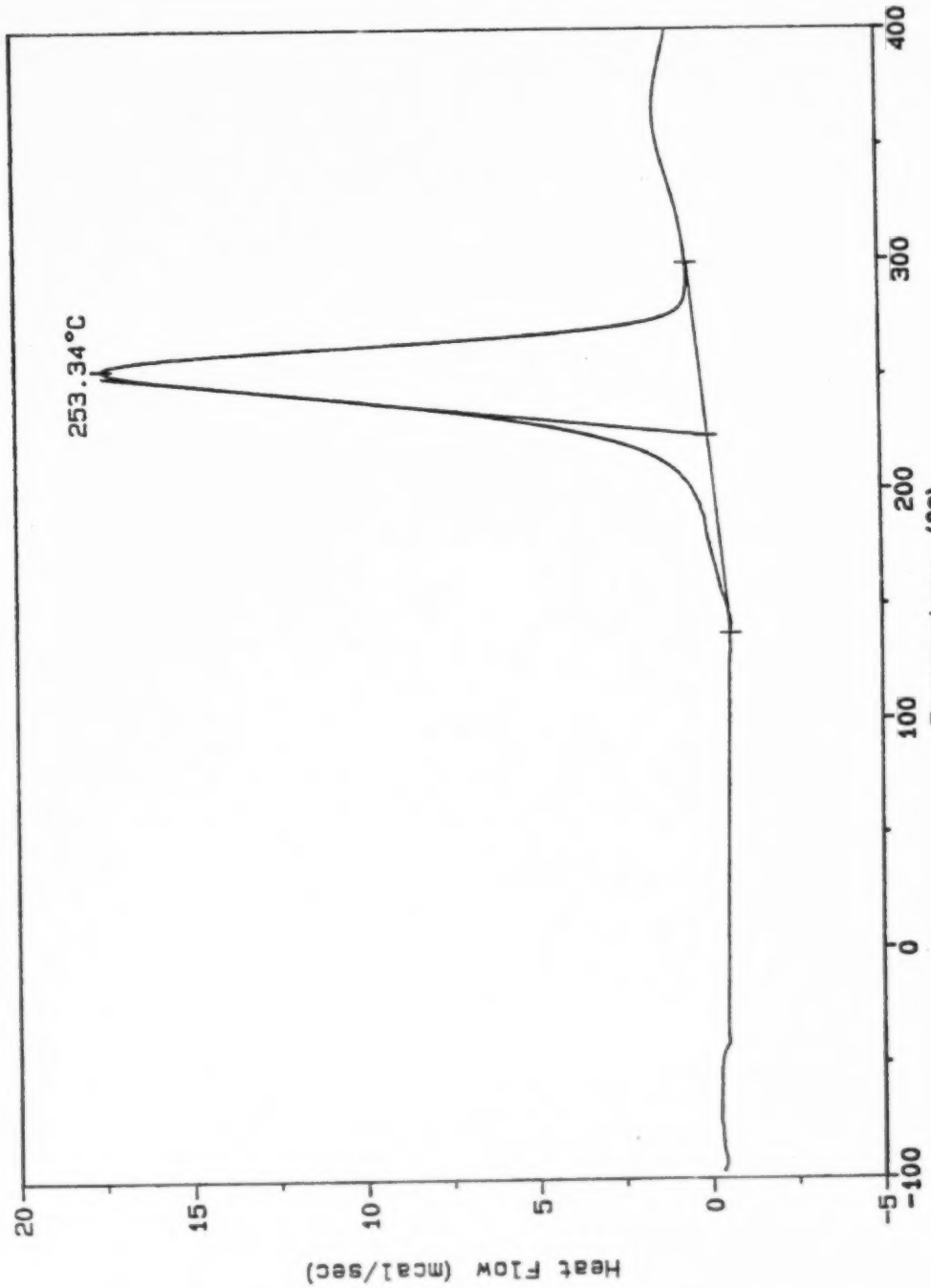

FIGURE 5 - DSC decomposition thermogram of Sample E38

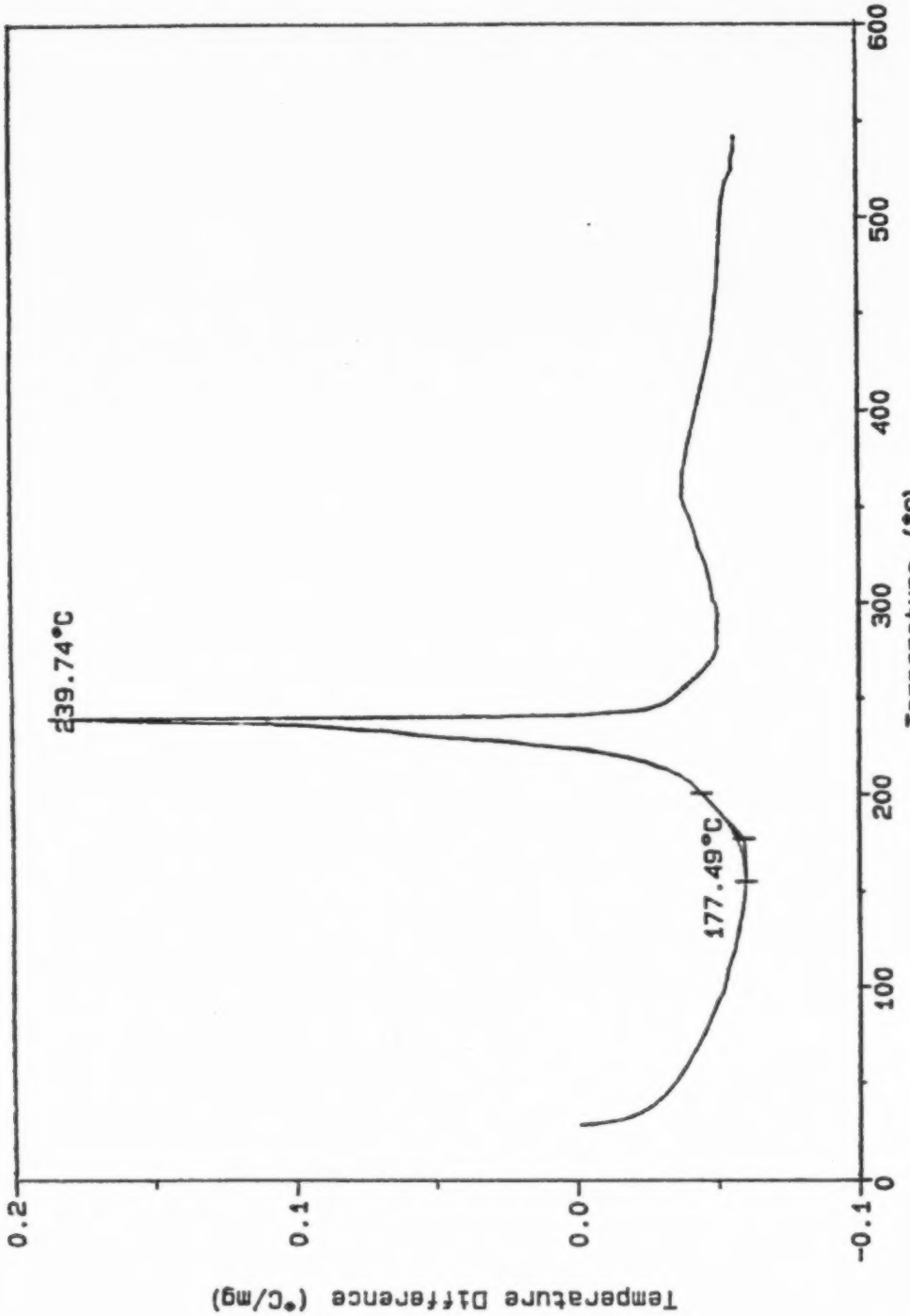

FIGURE 6 - DTA of Sample E133 (15 mg)

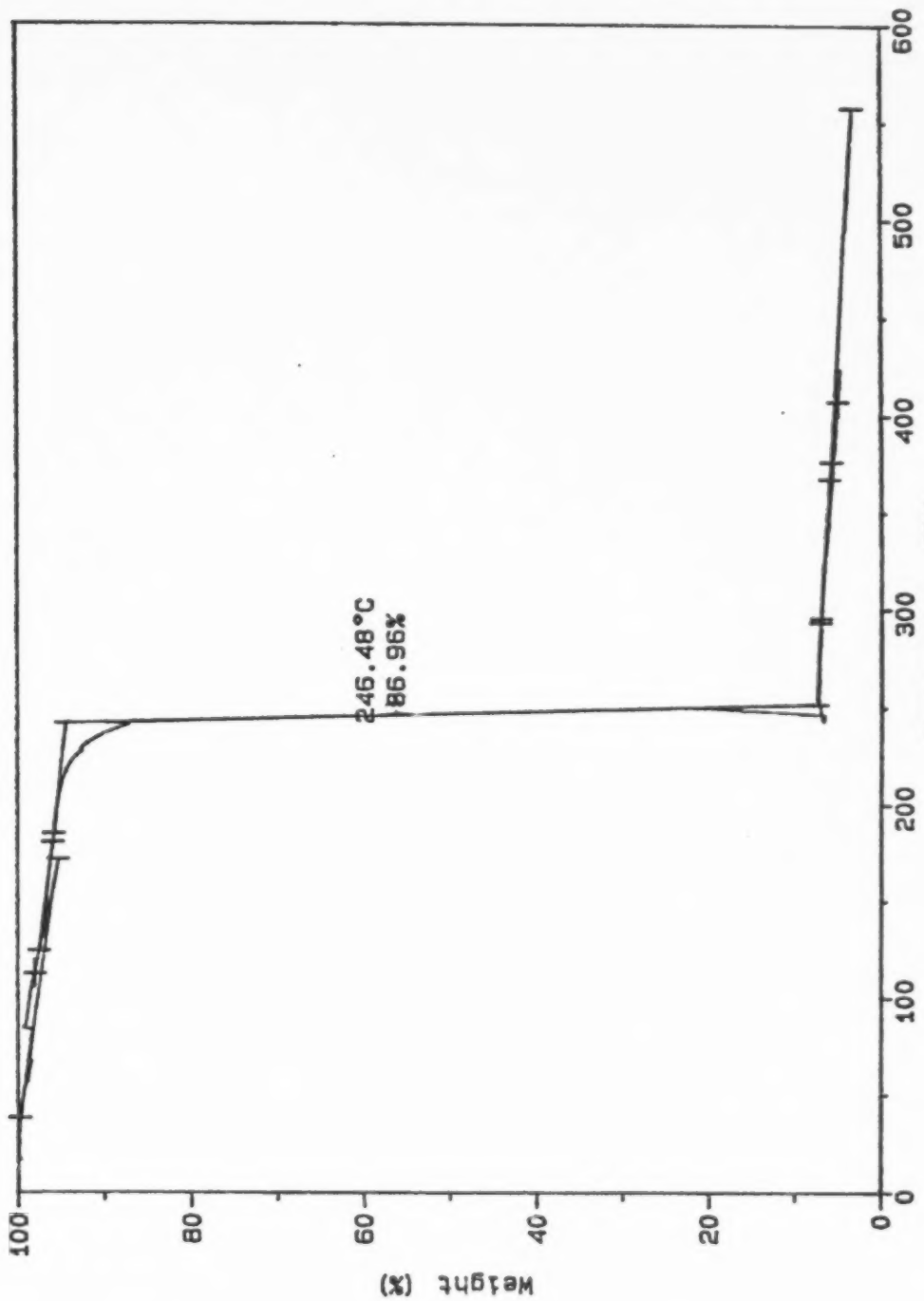

FIGURE 7 - TGA of Sample E133 (12 mg)

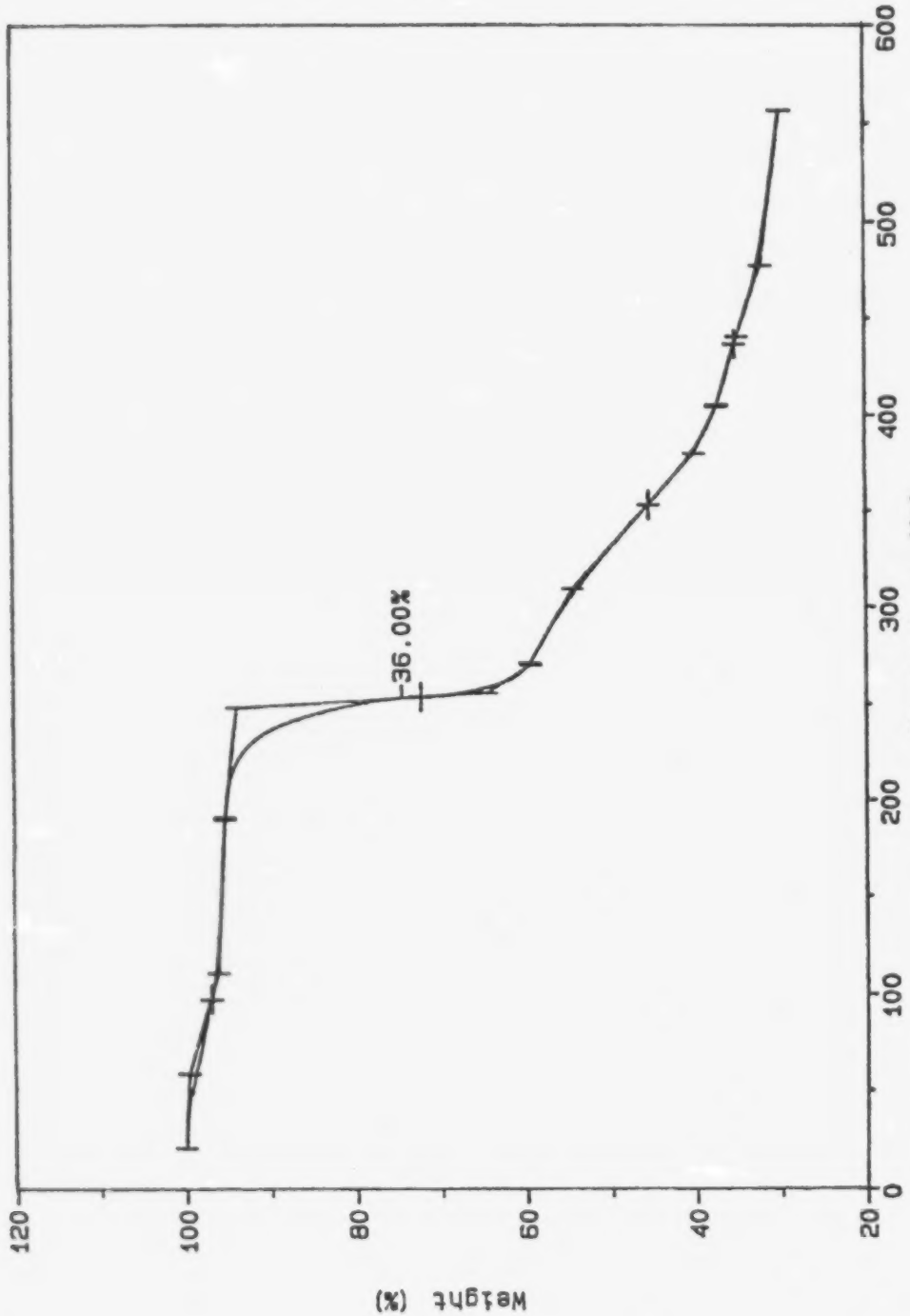

FIGURE 8 - TGA of Sample E147 (7 mg)

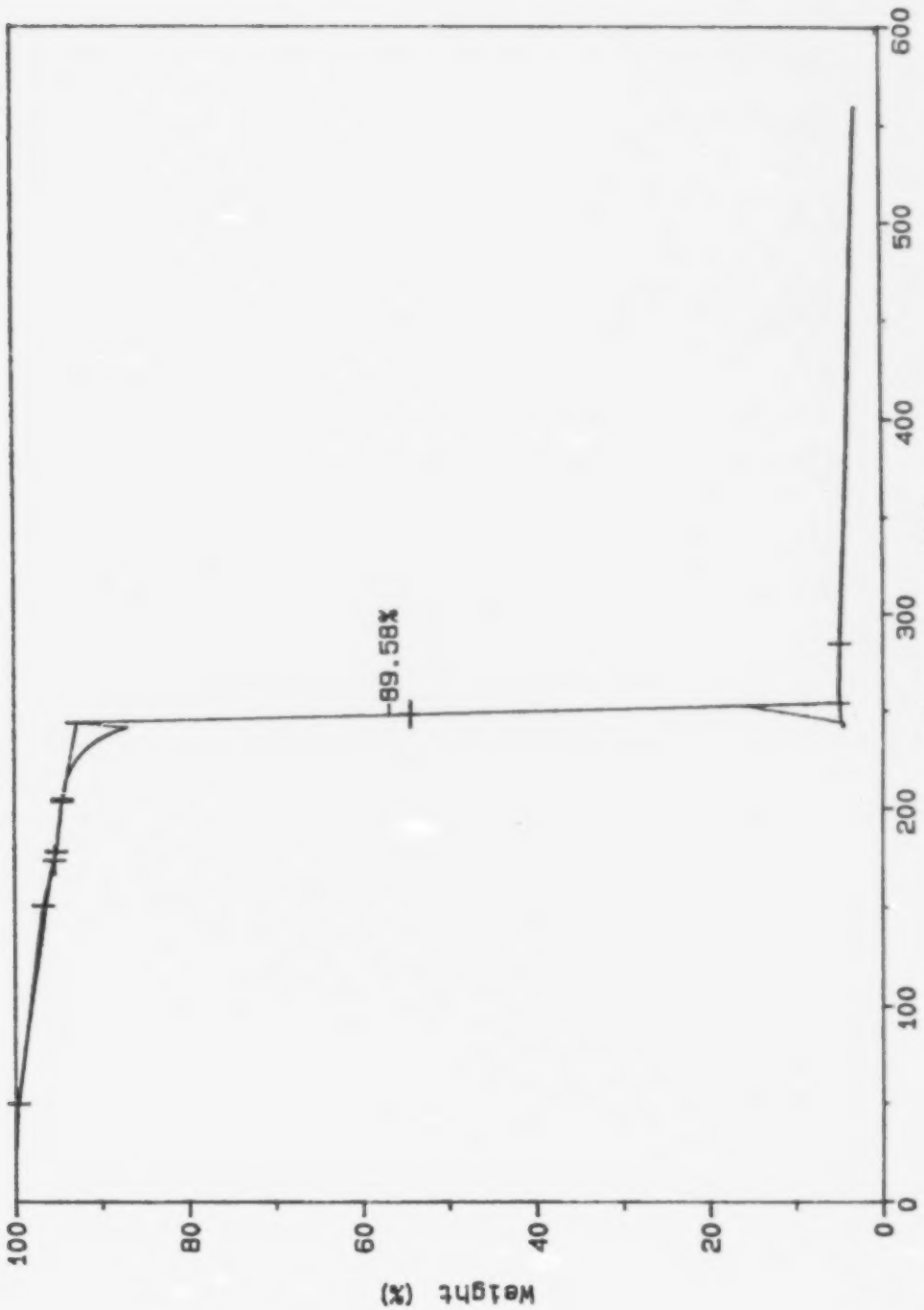

FIGURE 9 - TGA of Sample E147 (11 mg)

UNCLASSIFIED

INTERNAL DISTRIBUTION

DREV - R - 9512

1 - Deputy Director General
1 - Military Assistant
1 - Director Weapon Systems Division
1 - Director Command and Control Division
1 - Director Electro-Optics Division
6 - Document Library
1 - Dr. E. Ahad (author)
1 - Dr. R. Lavertu
1 - Dr. S. Thiboutot
1 - Dr. L.-S. Lussier
1 - Dr. S. Désilets
1 - Dr. G. Ampleman
1 - Mr. P. Twardawa
1 - Mr. P. Lessard
1 - Mr. C. Dubois
1 - Mrs. S. Villeneuve
1 - Mrs. F. Beaupré
1 - Mr. P. Brousseau
1 - Mr. C. Bélanger
1 - Mr. J. Angers
1 - Mrs. N. Gagnon

EXTERNAL DISTRIBUTION

DREV - R - 9512

2 - DSIS
1 - CRAD
2 - DRDL
1 - DACME-2
5 - ICI Explosives Canada
801 Richelieu Boulevard
McMasterville (Québec)
J3G 1T9
Attention: Dr. W.B. Evans
Mrs. J.A. Barna
Dr. P.G. Groeneweg
Dr. J. Leonard
Dr. M. Miskow

1 - Royal Military College
Kingston, Ontario
K7L 2W3
Attention: Dr. V.T. Bui
Department of Chemistry and
Chemical Engineering

1 - Bristol Aerospace Ltd.
P.O. Box 874
Winnipeg, Manitoba
Canada, R3C 2S4
Attention: Mr. D. Alexander

1 - Canadian Embassy
501 Pennsylvania Ave, N.W.
Washington, D.C. 20001-2114
U.S.A.
Attention: Dr. J. Lavigne
Assistant Attaché
Canadian Defence Liaison Staff

UNCLASSIFIED
SECURITY CLASSIFICATION OF FORM
(Highest classification of Title, Abstract, Keywords)

DOCUMENT CONTROL DATA

1. ORIGINATOR (name and address)

DREV
2459, Pie XI Blvd., North
Val-Bélair, Quebec, Canada, G1K 3W0

2. SECURITY CLASSIFICATION
(Including special warning terms if applicable)

UNCLASSIFIED
Distribution limited to DND & Canadian Contractors

3. TITLE (Its classification should be indicated by the appropriate abbreviation (S,C,R or U)
CHARACTERISTICS OF SECOND GENERATION BRANCHED GAP

4. AUTHORS (Last name, first name, middle initial. If military, show rank, e.g. Doe, Maj. John E.)

AHAD, Elie

5. DATE OF PUBLICATION (month and year)	6a. NO. OF PAGES	6b. NO. OF REFERENCES
December 1995	19	23

7. DESCRIPTIVE NOTES (the category of the document, e.g. technical report, technical note or memorandum. Give the inclusive dates when a specific reporting period is covered.)

Report

8. SPONSORING ACTIVITY (name and address)

DREV, 2459, Pie XI Blvd., North, Val-Bélair, Quebec, Canada, G1K 3W0

9a. PROJECT OR GRANT NO. (Please specify whether project or grant)	9b. CONTRACT NO.
2312C19A	

10a. ORIGINATOR'S DOCUMENT NUMBER	10b. OTHER DOCUMENT NOS.
DREV - R - 9512	N/A

11. DOCUMENT AVAILABILITY (any limitations on further dissemination of the document, other than those imposed by security classification)

- ☐ Unlimited distribution
- ☐ Contractors in appoved countries (specify)
- ☐ Canadian contractors (with need-to-know)
- ☐ Government (with need-to-know)
- ☒ Defence departments
- ☐ Other (please specify) :

12. DOCUMENT ANNOUNCEMENT (any limitation to the bibliographic announcement of this document. This will normally correspond to the Document Availability (11). However, where further distribution (beyond the audience specified in 11) is possible, a wider announcement audience may be selected.)

Distribution limited to DND

UNCLASSIFIED
SECURITY CLASSIFICATION OF FORM

UNCLASSIFIED
SECURITY CLASSIFICATION OF FORM

13. ABSTRACT (a brief and factual summary of the document. It may also appear elsewhere in the body of the document itself. It is high desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall begin with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (S), (C), (R), or (U). It is not necessary to include here abstracts in both official languages unless the text is bilingual).

This report describes the solution properties and thermal characteristics of second generation branched glycidyl azide polymer (GAP). The GAP products obtained in different solvents have the same viscosity-molecular weight and functionality-molecular weight relationships. The properties of branched GAP synthesized without using any polyol in the reaction and the characteristics of the polymers prepared without cleaving agent are also reported. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) thermograms, the glass transition temperature (Tg) as well as the heats of combustion (Hc), formation (Hf) and decomposition (Hd) of branched GAP are also presented. The correlation between the vacum thermal stability (VST) of the GAP product and the synthesis parameters is also discussed. The effects of stabilizers, additives and the purification procedure (extraction or water precipitation) on the properties of the GAP product are also presented.

14. KEYWORDS, DESCRIPTORS or IDENTIFIERS (technically meaningful terms or short phrases that characterize a document and could be helpful in cataloguing the document. They should be selected so that no security classification is required. Identifiers, such as equipm model designation, trade name, military project code name, geographic location may also be included. If possible keywords should be selected from a published thesaurus. e.g. Thesaurus of Engineering and Scientific Terms (TEST) and that thesaurus-identified. If it is n possible to select indexing terms which are Unclassified, the calssification of each sould be indicated as with the title.)

Glycidyl azide polymer
GAP
Branched structure
Synthesis parameters
Cleaving agent
Polyol
Molecular weight
Equivalent weight
Hydroxyl functionality
Viscosity
Intrinsic viscosity
Heat of formation
Heat of combustion
Heat of decomposition
Peak temperature
Differential scanning calorimetry
Differential thermal analysis
Thermogravimetric analysis
Vacum thermal stability
Glass transition temperature
Water precipitation
Extraction
Adsorption chromatography columns
Stabilizers
Additives
Purification

154755

UNCLASSIFIED
SECURITY CLASSIFICATION OF FORM